192

PROPERTIES OF LACTOPRENE EV

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Milling characteristics and physical properties of a vulcanizable copolymer of 95% ethyl acrylate and 5% chloroethyl vinyl ether (Lactoprene EV) have been investigated. The polymer does not require preliminary breakdown on the mill and, when properly formulated, the stock may be compounded without difficulty. Tensile properties of lactoprene vulcanizates are well above a serviceable minimum, but the cured product exhibits low resilience on the formulations studied. In the field of specialty rubbers, the product possesses two outstanding properties—resistance to oils and to dry heat. In its resistance to organic solvents, Lactoprene EV compares favorably with butadiene-acrylonitrile copolymers. The heat resistance of the vulcanized polymer is markedly superior to that of any of the present diene synthetics.

In recent years the development of synthetic rubbers has progressed along many lines which have produced useful rubberlike polymers of widely divergent properties. As technological requirements became more stringent, the specialty rubbers, whose exceptional properties made them valuable for specific applications, were demanded.

A recently developed specialty rubber with new properties is the polyacrylic elastomer. Early work on the development of vulcanizable polyacrylic resins was first reported by Fisher and co-workers in 1944 (*1*). The generic name "lactoprene" was proposed for acrylic esters copolymerized with small amounts of a polyfunctional monomer.

Shortly thereafter it was demonstrated that saturated copolymers of ethyl acrylate and halogen-containing acrylic derivatives could be vulcanized with the aid of suitable curing agents (*8*). One of these, Lactoprene EV, a copolymer of 95% ethyl acrylate and 5% chloroethyl vinyl ether, has since been studied extensively; the results are reported in this paper.

The compounding recipes tested are merely suggestive, and only one loading, 50 parts SRF black, was used. Furthermore, no attempt was made to improve the resilience of the vulcanizates by the addition of plasticizers. These limitations on compounding ingredients were exercised to demonstrate the basic properties of the rubber.

Data on compounding and curing characteristics, as well as stress-strain properties of Lactoprene EV, are given. In addition, the effect of solvents, steam, and dry heat are discussed.

COMPOUNDING

The milling characteristics of acrylic polymer differ markedly from those of natural rubber and of the butadiene copolymer type of synthetic rubber. The ethyl acrylate polymer bands readily when placed on the compounding mill, and no initial breakdown is required. The crude polymer is plastic even on a cold mill, and there is a strong tendency for the stock to adhere to both rolls until the filler has been incorporated. Furthermore, unless a suitable release agent, such as stearic acid, is included in the compounding formula, the stock adheres to the back roll throughout the process. One or two parts of stearic acid per 100 parts of polymer are usually sufficient to cause the stock to cling to the front roll.

Formerly, it was customary in this laboratory to compound the acrylic polymers on a cold mill to reduce the tendency of the stock to adhere to both rolls. In a few cases the data to be presented were obtained with vulcanizates compounded on cold rolls. The effect of milling on the intrinsic viscosity of the raw polymer is shown in Figure 1. A cold, tight 6 × 12 inch laboratory mill complying with requirements of the American Society for Testing Materials (D15–41) was used; samples of the batch

Table I. Representative Compounding Formulas for Use with Lactoprene EV

Formula	A	B	C
Polymer G157	100	100	100
Red lead	...	10	...
Zinc oxide	...	5	...
Stearic acid	1	3	1
p-Quinone dioxime (GMF)	...	2	...
Tetramethylthiuram monosulfide	1	...	1
Triethylenetetramine	...	1	...
Trimene Base	1	...	...
Sulfur	2	...	2
SRF black	50	50	50

were removed at intervals and dissolved in toluene (0.05 gram of polymer per 100 ml. of solvent). Viscosity measurements were made in a modified Ostwald viscometer at 25° C. (*7*). As Figure 1 shows, the polymer is exceptionally sensitive to mechanical breakdown when masticated on a cold mill.

For this reason the milling procedure was modified so that present laboratory technique on 6 × 12 inch rolls approximates that recommended by the Rubber Reserve Company for GR-S, except for the following. The preliminary breakdown is omitted, and roll temperature is adjusted between 140° and 160° F. at the beginning. No cooling water is circulated, and the temperature is permitted to drift. When first banded on the warm mill, the polymer tends to split and adhere to both rolls. Addition of filler is begun immediately. Usually the filler is an SRF black to which has been added the stearic acid called for in the formula. By the time half the carbon black–stearic acid mixture has been added, the stock is clinging tightly to the front roll, and a smooth rolling bank is formed. At this point it is customary to make one $^3/_4$ cut from each side holding the stock until the bank disappears. The remainder of the black–stearic acid mixture is added, and again a $^3/_4$ cut is made from each side. Usually when 30 parts of black per 100 of polymer are required, 1 part of stearic acid is sufficient as a release agent. If 50 parts of black are used, 2 parts of stearic acid may be preferred. The vulcanizing agents and other ingredients are quickly added after the incorporation of filler. The stock is cut and lapped so that there are three $^3/_4$ cuts from each side; then the stock is rolled and passed endwise through the mill six times. It is then sheeted to the desired thickness and allowed to cool. The temperature of the stock removed from the mill is of the order of 175° to 185° F. The sheeted stock is comparatively smooth and glossy, and shrinkage is of the order of 33%.

The stock adheres firmly to the front roll until the first $^3/_4$ cuts are made and it is difficult to make these first cuts without momentarily stopping the mill. However, this difficulty may be obviated if the compounder prepares a master batch of the polymer, carbon black, and stearic acid as a leader. Since lactoprene does not require premastication, it is well suited to compounding in a Banbury mixer. If this is done, the stock remains on the front roll and is released without difficulty.

Whenever possible, the authors employ the master batch technique in compounding lactoprene. It is possible to utilize higher temperatures in incorporating the black, and the over-all mixing schedule is shortened. As a consequence, breakdown of the stock appears to be materially reduced.

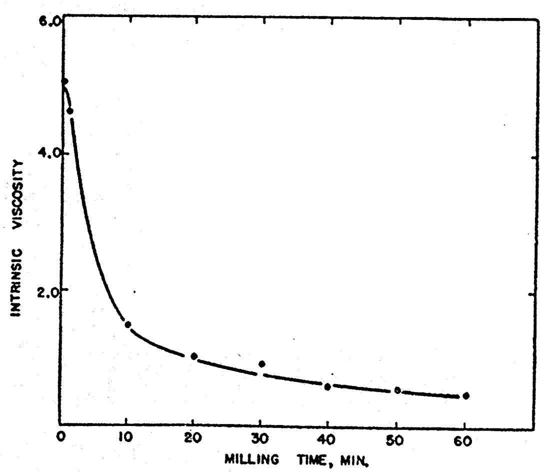


Figure 1. Change of Intrinsic Viscosity of Lactoprene EV with Time of Milling on Cold Rolls

Table II. Processing Characteristics of Representative Lactoprene EV Compounds

Compounding method	Roll Mill			Banbury Master Batch		
Stock number	ES 767	ES 768	ES 769	ES 771	ES 772	ES 773
Formula	A	B	C	A	B	C
Cumulative mixing time, min.						
To band	0.5	0.5	0.5	6.5[a]	6.5[a]	6.5[a]
Black started	1	1	1	6.5[a]	6.5[a]	6.5[a]
Black in	10.5	10.5	10.5	6.5[a]	6.5[a]	6.5[a]
Off mill	18.5	21	17.5	17.5	22.5	14.5
Mixing temperature, ° F.						
Front roll, start	150	150	150	150	150	150
Back roll, start	150	150	150	150	150	150
Batch, finish	192	194	189	175	175	183
Plasticity, mm.[b]						
Raw	8.2	8.2	8.2	8.2	8.2	8.2
Compounded	8.5	7.9	7.5	7.6	7.4	7.2
Mill shrinkage, %	29.2	21.8	33.3	34.4	29.2	27.1

[a] 6 minutes required for master batch.
[b] Williams, 5 kg., 10 minutes at 158° F.

The temperature of the Banbury mixer is maintained at 200° to 210° F. merely because the equipment is designed for use with steam at atmospheric pressure. During mixing the actual temperature of the stock rises to 350° F., as measured by a needle type pyrometer. Higher mixing temperatures have not been explored, but it is expected that they can be employed without serious thermal decomposition.

Three representative compounds of Lactoprene EV were prepared by the open mill and the master batch procedures suggested above. Test formulas A, B, and C are listed in Table I.

Formulas A and C are basically similar except that A includes the accelerator Trimene Base (triethyltrimethylenetriamine) to reduce the curing time. Formula B is a nonsulfur recipe which tends to produce a tight cure. Formula A is considered to be a general purpose recipe; the others are included to show the effect of formulation on specific properties of vulcanizates.

Processing characteristics of the three stocks (Table II) are such that the polymer bands readily on the mill and no breakdown is required; thus the incorporation of carbon black may be begun immediately. The time required for milling in the black is somewhat shorter than that required for other synthetic elastomers. Furthermore, the over-all milling time is comparatively short. The temperature of Lactoprene EV stocks tends to run high during compounding. High milling temperatures serve to plasticize the polymer and thus improve processability. Williams plasticity values for these three stocks are also shown in Table II. The plasticity tests were performed at 70° C. under standard conditions, according to specification D-2 for Government Synthetic Rubbers, July 1, 1946. As determined by a recommended method (*5*), the mill shrinkage of the stocks tested was of the same order as that obtained on a normal laboratory test batch of GR-S compounded by a standard formula (*5*).

CURING

Lactoprene EV stocks are slower in curing than the general purpose synthetics, although a satisfactory cure is obtainable in 30 to 120 minutes at 298° F. For commercial applications the

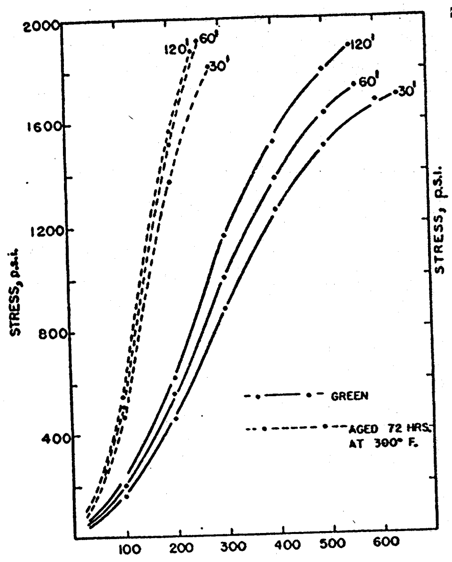
Table III. Typical Physical Properties of Lactoprene EV Vulcanizates

Cure at 298° F., Minutes	Stock A: ES 767, schedule I[a]	Stock A: ES 771, schedule II[b]	Stock B: ES 768, schedule I	Stock B: ES 772, schedule II	Stock C: ES 769, schedule I	Stock C: ES 773, schedule II
			Tensile Strength, Lb./Sq. In.			
30	1500	1700	1390	1360	...	...
60	1580	1740	1650	1650	1070	1420
90	1620	1870	1780	1870	1190	1600
120	1640	1890	1850	1960	1280	1720
180	...	...	...	...	1320	1780
			Elongation, %			
30	540	640	410	550	...	...
60	480	560	320	360	820	860
90	470	560	260	290	700	720
120	440	550	200	230	610	690
180	...	...	...	...	580	660
			Modulus at 200%, Lb./Sq. In.			
30	600	460	840	630	...	...
60	680	560	1300	1190	310	210
90	740	610	1600	1620	380	280
120	830	610	1850	1870	430	310
180	...	...	...	...	500	410
			Durometer Hardness (30 Seconds)			
30	51	49	60	55	...	...
60	53	49	69	62	45	42
90	54	50	74	70	46	45
120	54	50	78	75	48	45
180	...	...	...	...	49	47
			Break Set, %			
30	12	15	9	18	...	...
60	11	13	10	15	16	17
90	12	16	12	16	12	13
120	11	16	11	15	10	13
180	...	...	...	...	11	14
			Bashore Rebound, %			
30	2	1	3	3.5	...	...
60	2	1	4	4	1	1
90	2	1	4	4.5	1.5	1
120	2	1	4.5	5	2	1
180	...	...	...	...	1.5	1
			Compression Set[c] at 77° F., %			
65	...	...	14.4	...	...	...
120	19.3	...	...	...	...	...
180	...	...	...	...	13.3	...
			Compression Set[c] at 158° F., %			
65	...	...	20.8	...	...	...
120	50.8	...	...	...	...	...
180	...	...	...	...	39.5	...
			Compression Set[c] at 300° F., %			
65	....	...	86.0	...	...	...
120	88.0	...	...	...	...	...
180	....	...	...	...	66.6	...

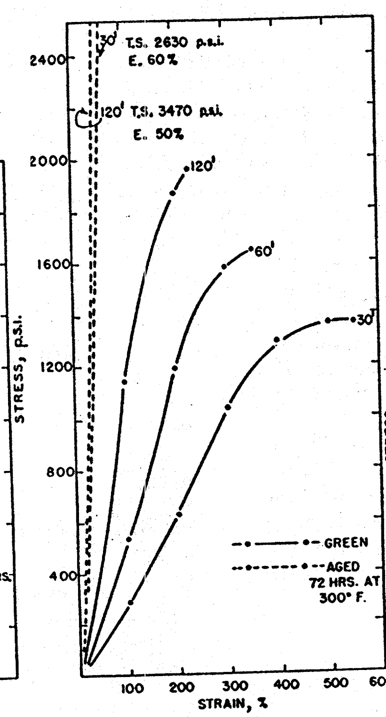
[a] Schedule I, compounding on roll mill throughout.
[b] Schedule II, compounding master batch in Banbury.
[c] Deflection, 40%; A.S.T.M. specification D395–40T, method B.

curing temperature may be raised to 325° F. for more rapid curing. In some instances the use of more highly accelerated curing recipes is possible (2). If Lactoprene EV stocks are given a prolonged cure, they eventually exhibit reversion of properties in a manner similar to natural rubber. However, the cure required to demonstrate this reversion is 24 hours or more at 298° F., depending upon the vulcanizing agent used. The time required for optimum cure based upon maximum tensile strength and modulus is correspondingly long. Usually lactoprene stocks are purposely undercured for practical reasons, such as reducing curing time and improving heat resistance.

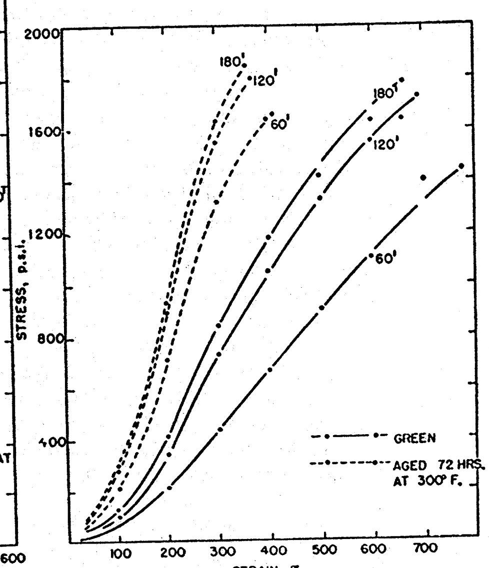
Undercured vulcanizates exhibit a strong tendency to adhere to the mold, and it is advantageous to employ a mold lubricant whenever possible. Most commercial rubber mold lubricants are unsatisfactory for use with lactoprene. They not only fail to lubricate, but also leave the vulcanizate with a dull surface, which suggests that the mold lubricant is absorbed by the rubber. Carnauba wax is moderately satisfactory as a mold lubricant.



A. Lactoprene EV, ES 771



B. Lactoprene EV, ES 772



C. Lactoprene EV, ES 773

Figure 2. Stress-Strain Properties of Three Lactoprene Stocks

The curing time in minutes, at 298° F., is indicated on each curve.

The specimen tested was a laboratory-prepared aqueous emulsion of the wax in kerosene (0.7% nonvolatile). Somewhat better results were obtained with an industrial finishing wax (Industrial Finish No. 1435, Johnson and Son, Inc.) diluted with distilled water to equivalent concentration.

The most satisfactory results were obtained with a lubricant compounded on the following recipe: Wax emulsion (12%), 5 parts; triethylenetetramine, 5 parts; and water, 90 parts. The mold lubricant is used sparingly and does not have any noticeable effect on the properties of the vulcanizate. The triethylenetetramine apparently causes a surface cure of the stock which assists in breaking the bond. Other curing agents for lactoprene, such as Trimene Base, may be substituted for the triethylenetetramine.

TENSILE PROPERTIES

Tensile properties of the three vulcanizates compounded by formulas A, B, and C, respectively, are presented in Table III. Both the open mill and Banbury master batch procedures were used. Tensile tests were conducted according to A.S.T.M. specification D412–41, and compression set according to specification D395–40T, method B. The tensile strengths of Lactoprene EV stocks, in general, are lower than those obtainable for diene synthetic rubbers but are well above a serviceable minimum for many applications. The distensibility and hardness of Lactoprene EV vulcanizates vary with compounding recipe. In all cases the break set is comparatively low. The vulcanizates exhibit delayed elasticity to a high degree, as is evidenced by the rebound data. The compression set results are also of some interest, particularly those obtained at elevated temperatures. Compound B displays lower compression set at 158° F. (70° C.) than do stocks A or C. This is not surprising since stock B is more tightly cured than either A or C. At higher test temperatures (300° F.), the data are partially reversed. Here stocks A and B develop higher compression set than does C. It is likely that vulcanizates A and B are subject to considerable after-vulcanization so that compressed specimens tend to retain their deformation after release.

Figure 2 presents stress-strain curves for the three compounds A, B, and C, before and after aging in an air oven for 72 hours at 300° F. The curves for the unaged vulcanizates are of interest because they differ from those of natural rubber and most synthetic stocks. The unaged vulcanizates appear to yield and flow under stress, as evidenced by the downward concave shape of the latter portion of the curves. However, the curves are misleading on this point because the break set data (Table III) show the permanent deformation of Lactoprene EV vulcanizates to be low. A more plausible interpretation of the stress-strain data recognizes the scission and reforming of secondary-valence cross links which occur during the deformation of the specimen, as postulated by Tobolsky and co-workers (*12*).

Exposure to heat under the conditions indicated causes stiffening of the vulcanizates. However, formulas A and C produce vulcanizates which are still serviceable after 72 hours of aging at 300° F., whereas formula B tends to cause excessive hardening of a similarly aged vulcanizate (Figure 2*B*).

SOLVENT RESISTANCE

The molecular structure of acrylic polymers is sufficiently polar to suggest that a vulcanizate such as Lactoprene EV might possess superior resistance to some organic solvents. Experiment demonstrated that the polymer has extraordinary resistance to aliphatic hydrocarbons.

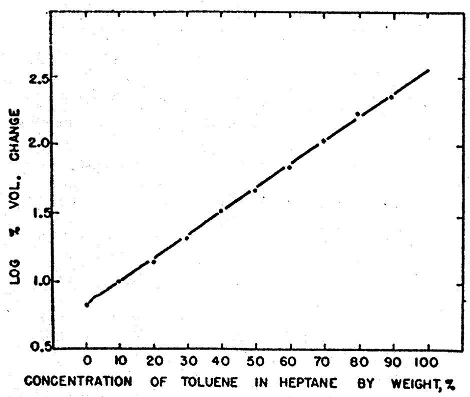


Figure 3. Equilibrium Volume Increase of Lactoprene EV in Mixtures of Toluene and Heptane at 77° F.

Tests on the solvent resistance of Lactoprene EV were conducted according to A.S.T.M. method A, designation D471–43T. Results obtained on three lactoprene stocks (Table IV) are compared with similar measurements on Hycar OR-15, Perbunan 26, and Perbunan 18 vulcanizates in Table V. The Hycar and Perbunan test slabs were optimum cures, but the Lactoprene EV specimens were undercured. As indicated earlier in this paper, lactoprene stocks cure slowly so that optimum cure (maximum modulus) may be 24 hours or more at 298° F.

Four swelling media were used—namely, reference fuels SR-6 and SR-10, Circo light process oil, and steam. Specimens immersed in SR-6, SR-10, and Circo oil were maintained at 77° F. for 168 hours; those exposed to steam were held at 212° F. for the same period. Physical tests were conducted at 77° F. and 50% relative humidity. With one exception the swollen volume figures are equilibrium values; Lactoprene EV samples immersed in steam continued to swell beyond the test period.

The volume increase of each of the lactoprene vulcanizates is greater than that of the Hycar OR-15 and slightly less than that of the Perbunan 26 stock in the two reference fuels, SR-6 and SR-10. The tensile properties of the lactoprene stocks suffered a greater percentage reduction in SR-6 than did those of the controls. The swelling of Lactoprene EV in aromatic hydrocarbons is appreciable, but it may be reduced through the use of increased loading and plasticizers. Swelling in SR-10 and Circo light process oil, on the other hand, is negligible; Lacto-

Table IV. Formulas for Three Lactoprene Stocks

Formula	ES 778	ES 779	ES 780	Hycar OR-15[a], 1275-HCR-138	Perbunan 26[b], 8925–1	Perbunan 18[b] 8925–2
Polymer	100	100	100	100	100	100
Zinc oxide	...	5	...	5	5	5
Red lead	...	10	...	...	...	...
Stearic acid	1	3	1	1	1	1
Dibutyl phthalate	...	...	...	10	...	...
Coumarone-indene resin (m.p. 20–30° C.)	...	...	...	10	...	...
SRF black	50	50	50	65	75	75
Sulfur	2	...	2	1.5	1.5	1.5
Tetramethylthiuram monosulfide	1	...	1	...	...	...
p-Quinone dioxime	...	2	...	...	...	...
Diphenylguanidine	...	...	...	0.2	...	...
Benzothiazyl disulfide	...	...	...	1.5	1	1
Triethylenetetramine	...	1	...	...	...	...
Trimene Base	1	...	...	...	...	...
Curing time, min.	120	120	120	45	60	60
Curing temperature, ° F.	298	298	298	310	287	287

[a] Cured A.S.T.M. test slabs supplied by Hycar Chemical Company.
[b] Cured A.S.T.M. test slabs supplied by Esso Laboratories.

Table V. Effect of Standard Media on Physical Properties of Lactoprene EV Vulcanizates[a]

	Reference Fuel SR-6 at 77° F.[b]					Reference Fuel SR-10 at 77° F.[c]					Circo Light Process Oil at 77° F.[d]					Steam at 212° F.				
	Lactoprene EV			Hycar OR-15, 1275-HCR-138	Perbunan 26, 8925-1	Lactoprene EV			Hycar OR-15, 1275-HCR-138	Perbunan 26, 8925-1	Lactoprene EV			Hycar OR-15, 1275-HCR-138	Perbunan 18, 8925-2	Lactoprene EV			Hycar OR-15, 1275-HCR-138	Perbunan 18, 8925-2
	ES 778	ES 779	ES 780			ES 778	ES 779	ES 780			ES 778	ES 779	ES 780			ES 778	ES 779	ES 780		
Volume, %																				
Original	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Immersed, 168 hr.	148	141	149	121	157	103	102	103	100	114	100	100	100	100	111	200	146	194	111	122
Recovered, 4 hr.	130	127	131	115	127	103	102	102	100	113	100	100	100	100	111	192	143	185	110	120
Tensile strength, lb./sq. in.																				
Original	1770	2370	1520	2560	2980	1770	2370	1520	2560	2980	1770	2370	1520	2560	2740	1770	2370	1520	2560	2740
Immersed, 168 hr.[e]	510	920	440	1350[f]	1150	1780	2010	1450	2440	2660	1970	2030	1450	2550	2570	440	1220	430	2390	2460
Recovered, 4 hr.[e]	760	1270	700	1510	2110	1750	2010	1420	2150	2580	1900	2070	1540	2740	2530	560	1070	490	2550	2410
Elongation, %																				
Original	450	160	680	510	410	450	160	680	510	410	450	160	680	510	420	450	160	680	510	420
Immersed, 168 hr.	240	200	360	310[f]	220	500	210	730	450	380	460	150	650	470	410	150	80	150	320	270
Recovered, 4 hr.	310	220	530	340	330	450	210	700	410	400	470	210	700	520	390	150	50	150	340	260
Hardness																				
Original	51	84	45	56	69	51	84	45	56	69	51	84	45	56	66	51	84	45	56	66
Immersed, 168 hr.	44	55	35	55	55	49	75	43	58	61	50	82	46	62	61	48	81	47	65	63
Recovered, 4 hr.	44	57	37	54	60	48	78	41	53	63	50	80	42	61	61	51	83	48	65	66
Rebound, %																				
Original	1.0	6.0	0.5	24	28	1.0	6.0	0.5	24	28	1.0	6.0	0.5	24	40	1.0	6.0	0.5	24	40
Immersed, 168 hr.	66	59	58	58	62	1.5	5.0	1.0	20	52	0.5	9.0	0.5	11	46	7.5	19.0	6.5	12	45
Recovered, 4 hr.	46	49	49	48	58	0.5	6.0	1.0	26	51	0.5	6.0	0.5	19	43	6.0	20.0	5.0	10	43

[a] Test method used was A.S.T.M. designation D471–43T.
[b] Reference fuel, diisobutylene plus 40% aromatics, supplied by Stanco Distributors.
[c] Reference fuel, diisobutylene, supplied by Stanco Distributors.
[d] A.S.T.M. Oil No. 3 (D471–43T) supplied by Sun Oil Company.
[e] Tensile strength calculated on basis of swollen cross section.
[f] Result from one dumbbell only.

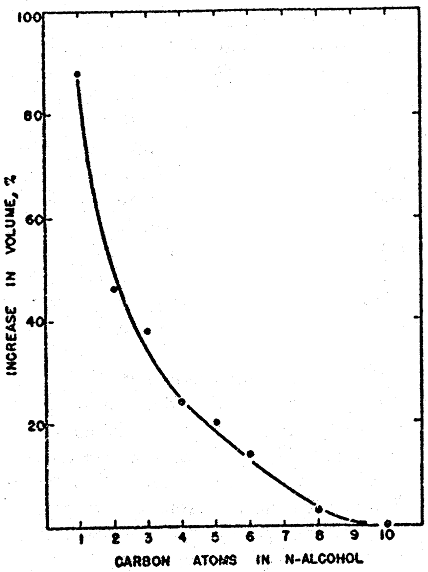


Figure 4. Volume Increase of Lactoprene EV in Normal Alcohols

prene EV compares favorably in volume increase and retention of physical properties with the Hycar and Perbunan stocks.

The effect of steam on dimensional stability and physical properties of lactoprene vulcanizates is also shown in Table V. Improvement in steam and water resistance may be expected from the use of plasticizers or metal oxide loading; experiments are still in progress and results are not available at this time.

A.S.T.M. method B, designation D471–43T, was also used for a simplified evaluation of solvent resistance. Essentially, this method consists in measuring the extension of 100 × 1.6 × 1.9 mm. specimens immersed in the test solvent for 3 days. The volume increase, ΔV, is expressed as function of change in length, ΔL (*2*).

Using this method, the swelling of several oil-resistant synthetic rubbers in standard reference fluids was measured, and the results are shown in Table VI. The heptane and toluene-hep-

Table VI. Comparison of Percentage Increase in Volume of Representative Synthetic Rubbers with Lactoprene EV after 3 Days' Immersion at Room Temperature[a]

Sample	Circo Light Process Oil	SR-10	SR-6	Heptane	50% Heptane, 50% Toluene, by Vol.
Thiokol ST	0	0	12	3	17
Thiokol FA	0	0	11	3	19
Neoprene 1109N-85	8	19	110	21	140
Perbunan 26, 8925-1	3	12	52	12	68
Perbunan 18, 8925-2	9	21	82	22	105
Hycar OR-15, 1275HCR-138	0	0	17	1.5	26
Hycar OR-25, 1275HCR-128	0	3	28	6.1	44
Lactoprene EV 2081 60/50[b]	0	1.5	37	1.5	42

[a] Method of Garvey (*2*), designation D471–43T, method B.
[b] After immersion in Circo light process oil for 3 days at 212° F., the volume increase was 3%.

Table VII. Volume Increase of Lactoprene EV, G-157 (2169), Immersed for 72 Hours at 77° F. in Various Hydrocarbons

Solvent	Volume Increase, %	Solvent	Volume Increase, %
Skellysolve B	7.6	Benzene	413.1
Skellysolve C	6.1	Toluene	333.1
Skellysolve F	6.1	Ethylbenzene	287.0
Skellysolve L	3.0	Diisopropylbenzene	24.2
Hexane	4.5	Triisopropylbenzene	0
Heptane	0		

tane mixtures are included as checks on the SR-10 and SR-6, respectively. The Lactoprene EV stock (2081) used in this test was compounded and cured as follows: Lactoprene EV, G-157, 100; litharge, 8; accelerator 808, 3; and SRF black, 50; cured, 60 minutes at 298° F. The results show that Lactoprene EV compares favorably in dimensional stability with the other oil-resistant rubbers tested. The neoprene sample was a laboratory composition and does not necessarily represent a commercial product.

The system toluene-heptane was investigated more fully, and the results are shown in Figure 3. Compounding and curing data on the test specimens (ES 778) are given in Tables IV and V. The marked effect of aromatic hydrocarbons on the type of acrylic polymer described is obvious. Perhaps it is of interest that the logarithm of volume increase *vs.* concentration by weight of toluene in the toluene-heptane mixture yields a straight-line plot. All points, with the possible exception of the lowest, are equilibrium values. Additional data on the swelling of Lactoprene EV in various hydrocarbons are shown in Table VII. As expected, the volume increase in aromatic hydrocarbons is large, and that in the paraffinic hydrocarbons is exceptionally small. The benzene, toluene, ethylbenzene, isopropylbenzene series is of some interest. In the presence of sufficiently bulky side groups the swelling effect of the aromatic nucleus is completely lost.

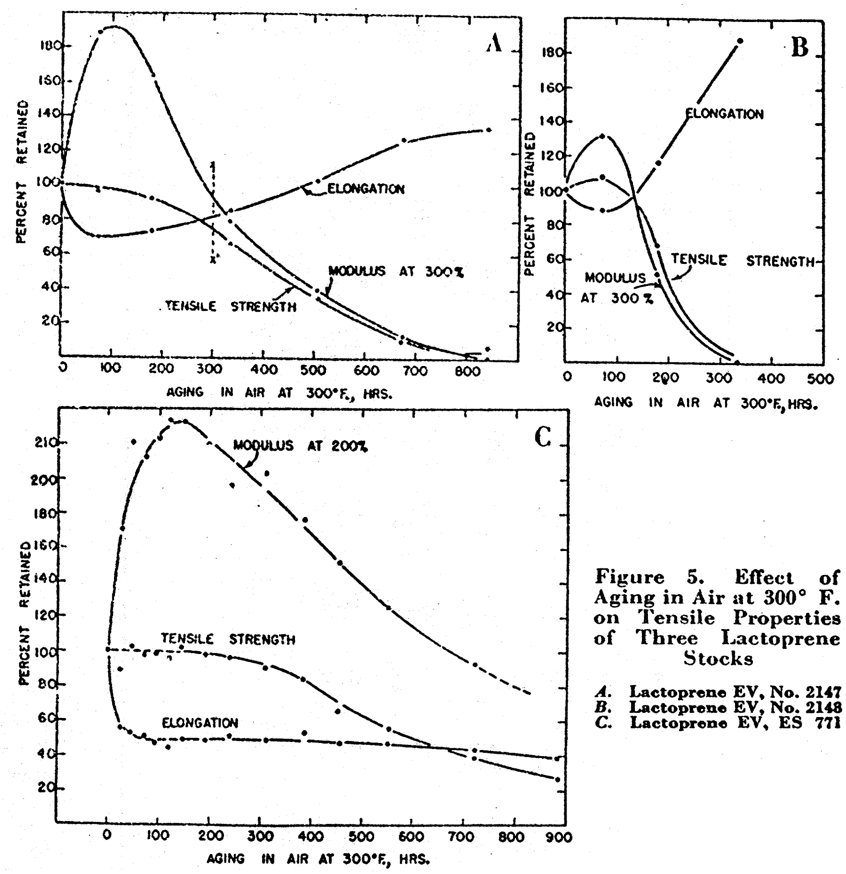


Figure 5. Effect of Aging in Air at 300° F. on Tensile Properties of Three Lactoprene Stocks

A. Lactoprene EV, No. 2147
B. Lactoprene EV, No. 2148
C. Lactoprene EV, ES 771

The swelling of Lactoprene EV for 3 days at 77° F. in various alcohols is shown in Figure 4 and Table VIII. In the normal alcohol series the swelling is inversely related to the number of carbon atoms, ending with *n*-decanol which produces no apparent effect. Branched-chain alcohols cause greater swelling, as shown with 4-, 6-, and 8-carbon alcohols (Table VIII). Cellosolves and Carbitol also cause marked swelling of the vulcanizate.

HEAT RESISTANCE

The stability of Lactoprene EV vulcanizates in the presence of dry heat is outstanding in comparison with that of natural rubber and the butadiene copolymer type of synthetic rubber. Except for Butyl rubber, the susceptibility of the diene synthetics to heat aging is believed to be related to their unsaturation. This has been demonstrated, for example, on heat-resistant stocks based on a 50-50 mixture of Hycar OR-15 and Perbunan (*9*), on GR-S compounds (*3, 6, 11*), on Butyl rubber (*4*), and others.

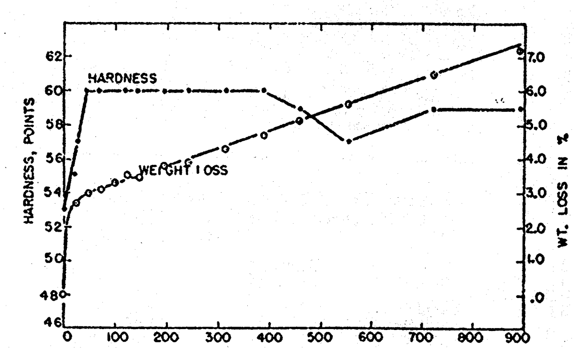


Figure 6. Effect of Aging in Air at 300° F. on Hardness and Weight of Lactoprene EV, ES 771

In a recent report on the relaxation of synthetic rubbers (*10*) at elevated temperatures, Mesrobian and Tobolsky postulated that the presence of double bonds or methyl groups in the polymer chain tends to favor degradation. They reported that ester groups in the polymer chain, on the other hand, appear to be responsible for improved heat resistance. Data on the heat resistance of lactoprene vulcanizates gathered in this laboratory do not contradict this view.

Table IX shows heat aging results on a number of lactoprene compounds aged for 72 hours at 300° F. in a mechanical convection oven with the ports open. All stocks in this group were compounded on a cold mill and cured for 120 minutes at 312° F. prior to aging. The aged tensile data are reported in preference to the unaged properties because they are more representative of the various compounds. The change in each of the properties listed which occurs as a result of heat aging is given in per cent, plus or minus. Test results are arranged in order of ascending

TABLE VIII. VOLUME INCREASE OF LACTOPRENE EV, G-157 (2169) IMMERSED FOR 72 HOURS AT 77° F. IN VARIOUS ALCOHOLS

Solvent	Volume Increase, %	Solvent	Volume Increase, %
Methanol	88.4	*n*-Octyl alcohol	3.0
Ethanol	40.5	Capryl alcohol	12.5
n-Propyl alcohol	38.6	*n*-Decanol	0
n-Butyl alcohol	24.2	β-Chloroallyl alcohol	553.9
Isobutyl alcohol	33.1	1,4-Dioxane	417.8
tert-Butyl alcohol	72.8	Methyl Cellosolve	230.8
n-Amyl alcohol	20.8	Ethyl Cellosolve	272.4
2-Methyl-1-pentanol	72.8	Isopropyl Cellosolve	137.9
n-Hexanol	14.1	Butyl Cellosolve	81.6
Cyclohexanol	10.8	Phenyl Cellosolve	333.1

Table IX. Tensile Properties, and Percentage Change of Each, for Lactoprene EV Compounds after Aging for 72 Hours at 300° F.

(The compounds are arranged in order of ascending per cent change of modulus at 300% elongation)

Stock No.	2152	2131	2094	2155	2134	2141	2101	2107	2148	2087	2132	2073	2147	2091	2098
Polymer	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulfur	2	2	1	2	2	2	1	1	2	1	2	2	2	1	1
Furnex	...	...	30	...	...	...	30	30	...	30	...	...	30	30	30
Kosmos 40	30	30	...	30	30	30	...	...	30	...	30	30	...	...	...
Tepidone	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Butasan	...	1	...	...	...	...	...	...	...	...	...	...	...	...	...
Monex	...	...	2	...	...	...	2	2	...	2	...	1	1	...	2
Activex	...	...	...	1	...	...	...	...	...	...	...	...	...	...	...
Selenac	...	...	...	...	1	...	...	...	...	...	...	...	...	...	...
Pipsolene	...	...	...	...	...	1	...	...	1	...	...	...	...	...	...
Iron resinate	...	...	...	...	...	...	1	...	...	...	...	...	...	...	...
Cobalt resinate	...	...	...	...	...	...	...	1	...	...	...	...	...	...	...
Iron oxide	...	...	...	...	...	...	...	...	...	1	...	...	...	...	...
R-2 crystals	...	...	...	...	...	...	...	...	...	...	1	...	...	...	...
Tuads	...	...	...	...	...	...	...	...	...	...	...	...	...	2	...
Vultac No. 3	...	...	...	...	...	...	...	...	...	...	...	...	...	...	6
Tensile strength															
Aged, lb/sq. in.	950	850	920	1270	1250	1360	880	1140	1790	1030	1660	1730	1360	1310	1370
Change, %	−45	−41	−39	−21	−18	−7	−32	−10	+7	−25	+14	+5	−8	−8	−2
Elongation															
Aged, %	599	610	490	580	440	420	310	370	380	370	300	440	430	390	340
Change, %	+4	+11	−22	−3	−24	0	−33	−21	−12	−31	−14	−28	−31	−38	−37
Modulus at 300%															
Aged, lb./sq. in.	400	320	390	530	600	890	870	810	1400	780	1680	1040	790	880	1250
Change, %	−41	−26	−22	−4	+3	+2	+22	+31	+31	+32	+37	+65	+88	+110	+131
Hardness															
Aged	44	44	39	52	50	49	50	48	51	50	58	50	44	51	64
Change, %	−2	−2	−11	+16	+9	−2	+4	0	0	+6	+16	+11	+13	+16	+33

percentage change of modulus at 300% elongation. Thus, specimens on the left-hand side of the table whose change in modulus is negative exhibit other signs of reversion such as reduction in tensile strength and hardness. Conversely, those on the right, which develop a higher modulus on aging, exhibit stiffening and shortening.

In most of these tests only one aging period of 72 hours at 300° F. was employed. However, in the case of stocks 2147 and 2148 longer aging periods were used to investigate the trend of tensile properties. The per cent retention of tensile strength, ultimate elongation, and modulus at 300% elongation, are plotted against time of aging for stock 2147 in Figure 5*A*. The tensile strength falls off slowly with time, whereas elongation decreases rapidly to a minimum and then rises again. Similarly, the modulus rises rapidly to a maximum and then falls off consistent with the reversion of tensile strength.

Discussion is facilitated by dividing Figure 5*A* into two portions by the dotted line, x-x'. For aging periods which fall to the left of this dividing line, the tensile properties of the vulcanizate are substantially unimpaired. To the right of the dividing line, however, the stock undergoes serious thermal decomposition. Except for rapid-curing stocks containing a large excess of free vulcanizing agent, lactoprene vulcanizates, in general, behave similarly to stock No. 2147 with respect to heat resistance.

Consider a stock which is lower in per cent change of modulus (Table IX)—for example, stock No. 2148. Data are plotted in Figure 5*B* for this vulcanizate. Objectionable deterioration begins after 150 hours of aging at 300° F., whereas stock No. 2147 exhibits useful properties after 300 hours at the same temperature.

Thus, for a given aging period the sign of the per cent change of modulus indicates whether the stock is undergoing reversion—that is, whether the aging period selected terminates to the right or left of x-x'. For example, stock No. 2141 (Table IX) appears at first glance to be practically unchanged as a result of 72 hours of aging at 300° F. Without additional data one might anticipate that the durable life of this stock at 300° F. would be much longer than 72 hours. Actually this specimen has about reached the limit of its durable life, and 72-hour aging corresponds to the intersection of elongation and modulus curves in the neighborhood of x-x'.

The opposite condition is one in which the stock has been compounded on a suitable formula to give a tight cure. An example of this type of compound is vulcanizate ES 772, whose stress-strain characteristics are shown in Figure 2*B*. Presumably, free curing agent is present in the unaged vulcanizate so that curing continues during the heat aging period. This continuation of cure results in a stiff vulcanizate of high tensile strength and modulus and of low elongation. Furthermore, the cured stock shows no signs of reversion when aged for periods as long as 840 hours at 300° F. In this case conditions of cure are exaggerated to the extent that the tensile strength and elongation curves (on a plot of the type of Figure 5*A*) are permanently divergent, and for extreme periods of aging the stock is likely to become brittle.

Thus it is possible, through the proper selection of compounding formulas, to produce a vulcanizate which will exhibit reversion early in the aging period or resist this reversion indefinitely. As might be expected, heat resistant stocks of practical utility fall somewhere between these two limits.

The most heat resistant stock studied was ES 771 (Table III). Figure 5*C* summarizes retention of tensile properties, in per cent, against hours of exposure at 300° F. The effect of heat on Durometer hardness and specimen weight is shown in Figure 6. The Aeronautical Material Specification 3201 B for dry heat-resistant rubber requires that an acceptable stock retain 40% of its original tensile strength, 30% of its original elongation, and increase in Durometer hardness by not more than 20 points after 70 hours of exposure in air at 300° F. Stock ES 771 meets these requirements after more than 700 hours of aging at the specified temperature.

SUMMARY

The polyacrylic rubber Lactoprene EV possesses certain outstanding properties which recommend its use for many special applications. The resistance of vulcanized Lactoprene EV to swelling by lubricating oils and other aliphatic hydrocarbons is exceptionally good. However, the vulcanizate is susceptible to swelling by aromatic hydrocarbons, alcohols, and water. The compounding formulas used in these evaluations were purposely simplified to demonstrate the inherent properties of the vulcanized elastomer. It is anticipated that deficiencies in solvent resistance may be overcome by the use of specific formulations.

Perhaps the most striking property is the extreme resistance of the vulcanizate to dry heat. It is noteworthy that the development of maximum heat resistance in lactoprene stocks is, to a large degree, dependent upon suitable compounding ingredients.

ACKNOWLEDGMENT

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